

Review of ACP 2018-1308

Stefenelli et al.

Summary:

The authors burned wood in residential stoves under two burning conditions (flaming, smoldering) and with three different types of stoves. Emissions were sampled into a smog chamber and aged via OH-radical initiated oxidation. Several aging temperatures and VOC concentrations were explored. Resulting particles were measured with AMS and gas phase species with PTR-ToF. Gas-phase precursor species were sorted by chemical structure. SOA yields were measured. A box model was used to determine the volatility distribution of oxidation products. This was accomplished by iteratively adjusting the estimated concentrations of product species in various volatility bins, and the average enthalpy of vaporization, so that measured SOA concentrations best matched modeled concentrations. The relative contributions of different precursor VOC classes to SOA yield were determined using a genetic algorithm. The major results of the study are (1) smoldering and flaming conditions emit different primary VOCs, (2) cresols and phenols are important SOA precursors, (3) SOA yields increase at lower temperatures. However, the identification of which chemical classes of VOC are major SOA precursors was not consistent between different sets of experiments.

Overall I think that this work takes a promising approach to a difficult and important problem (SOA formation from biomass burning). The data set is interesting and the experimental techniques appropriate. However, there are some issues with disorganization in describing the analytical approach, the model implementation, and comparison of the effects of different variables (e.g. chemical composition, temperature, OH exposure) that make it difficult to follow the major conclusions and find information that could be useful for air quality modeling parameterization.

Major comments:

The analysis in this paper rests on the idea that there should be systematic differences in SOA yield between the six selected classes of SOA precursors. These classes are defined by structure: furans, PAH, unoxygenated aromatics, oxygenated aromatics, and two catch-all categories of other compounds with more and fewer than 6 carbon atoms. However, it is never clearly established why these six classes were chosen and so defined. Why not sort compounds by functionality (e.g. ketones, acids, diols, etc), O:C ratio, molecular weight, flaming vs. smoldering source, or some other characteristic? Why not handle each species separately? To summarize, the authors need to establish (1) why the lumping was necessary, and (2) why this particular differentiation of chemical characteristics should be expected to explain variability in SOA formation. Secondly, it appears that the individual species included in each chemical class were not the same for each experiment. This is a significant weakness of the analysis. The authors should strongly consider a more consistent and chemical meaningful approach to grouping compounds.

An additional point of concern is that multiple variables changed at same time: e.g. set 1 and set 2 experiments have different flaming/smoldering condition, different smog chamber temperatures, different OH exposure, and different VOC concentration. Is there a way to deconvolve these effects? The SOA yield of each experiment should best be compared at the same OH exposure.

Two papers using this dataset have been published previously (Bruns et al. 2016, 2017). In the introduction, the authors should more directly state the relationship of this work to the two previous papers and what new analysis is added.

The abstract could use some organizational editing, to clarify the major aims of the study, the analytical methods used to interpret the data, and the major results.

Specific comments:

It is not clearly described how different “flaming” and “smoldering” conditions were achieved in the two sets of experiments, and how the relative levels of flaming and smoldering were determined. The effect of temperature is not noted in the abstract.

Abstract: From the abstract it appears that one of the major conclusions is that flaming and smoldering conditions produce a different mix of VOCs, but this is not discussed in the paper.

Page 4 Line 1: These values don’t quite make sense to me; how is it possible that the contributions consistently add to more than 100%? Is this mass yield or carbon yield?

Page 4 Line 9: Which parameters?

Page 5 line 11: If relative humidity was constant, than actual water vapor mixing ratios were quite different between the three temperature conditions. Is this expected to have an effect? Why was this particular humidity condition chosen?

Page 5: What NO_x levels and NO_x:VOC ratios were present?

Page 6 line 15: AMS collection efficiencies can be substantially less than 1, especially for very low volatility and highly oxidized particles. A collection efficiency correction could change the conclusions of this work. Can you support the assumption of CE=1?

Page 8 line 27: Was photolysis of VOCs considered?

Page 9 Line 7: How were these 263 ions selected?

Eq. 4 and 5: Could the measured OA be simultaneously corrected for wall loss and dilution by dividing by the measured BC signal over time, normalized to 1 at t=0?

Page 11 Lines 30-Page 12 line 9: This needs to be better supported and more detailed. Each of the six main precursor classes was further subdivided into six volatility bins, and the average chemical properties were determined for each bin – is this correct? Was there a large range in #C, #H, #O within each bin? It is not entirely clear to me how the volatility bins were determined: was the volatility of each individual species determined, and species were then grouped into bins? Or were species first grouped using some other method, then the volatility of each group was determined?

Page 13 lines 1-7: Can you explain more clearly what mutation, crossover, and selection mean for the implementation of the genetic algorithm in this particular application? How does the algorithm actually identify the optimal set of parameters?

Page 14 lines 21-23: It should be stated more clearly before this point that the individual species contributing to each of the 6 chemical classes were not consistent between different experiments. The

inconsistency in chemical composition makes it extremely difficult to compare between different experiments or to draw conclusions about the SOA yield from different chemical classes.

Page 15 lines 4-6: Two groups of compounds could have substantially different distribution of OH reactivities and SOA formation potential, but similar average OH reactivity. The conclusion here is not well supported.

Technical corrections:

Abstract 8-10: Sentence is difficult to understand, please rephrase.

Page 5 line 49: should be sodium nitrite, NaNO_2

Eq. 1 Brackets for the sum term are missing